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Interaction Energies for the H-H_2 and $\text{H}_2\text{-H}_2$ System*

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Interaction energies for the H-H_2 and $\text{H}_2\text{-H}_2$ systems have been obtained by a semiempirical perfect-pairing procedure used previously. The results have been compared with interaction energies obtained from other sources and the agreement among the different curves is reasonably good. A brief discussion of the previous applications of this semiempirical scheme to other systems is included.

INTRODUCTION

A CALCULATION of the transport properties of a gas presupposes a knowledge of the interaction energies between the various species present in the gas. Hydrogen gas at temperatures of several thousand degrees will contain not only hydrogen molecules but also a fair amount of ground-state hydrogen atoms. Consequently, the atom-atom, atom-molecule, and molecule-molecule interactions must be known if one wants to obtain reliable results from a transport-property calculation. Hydrogen should serve as a particularly simple example for the calculation of transport properties of hot gases, and its transport properties are of some current interest for their own sake.¹

As two ground-state hydrogen atoms approach one

another, they can interact along either one of two potential curves, corresponding to the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ spectroscopic states of molecular hydrogen. Reasonably accurate curves for these interactions are known,²⁻⁵ but the curves for the interactions such as H-H_2 and $\text{H}_2\text{-H}_2$ are not well known over a range of distance corresponding to interaction energies of about a volt or less. This latter range is the important one in determining high-temperature properties.

Previously we have used the valence-bond scheme of perfect pairing⁶ to generate atom-molecule and mole-

² J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Mol. Spectroscopy* **3**, 17 (1959).

³ H. M. James, A. S. Coolidge, and R. D. Present, *J. Chem. Phys.* **4**, 187 (1936).

⁴ A. Dalgarno and N. Lynn, *Proc. Phys. Soc. (London)* **A69**, 821 (1956).

⁵ R. J. Fallon, E. A. Mason, and J. T. Vanderslice, *Astrophys. J.* **131**, 12 (1960).

⁶ C. A. Coulson, *Valence* (Oxford University Press, London, 1952), pp. 166-171.

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¹ J. J. Newgard and M. Levoy, *Sci. American* **200**, 46 (1959).

cule-molecule interactions from a knowledge of atom-atom interactions. The results so obtained agreed well with the available experimental data.⁷⁻¹⁰ It seemed reasonable to suppose that we might use the same semiempirical procedure to calculate the interaction energies for the H-H₂ and H₂-H₂ systems from a knowledge of the H-H interactions. These systems also serve as an especially simple case for the further testing of this semiempirical scheme. Curves for these interactions have been obtained and are compared with results obtained by other methods.

METHOD AND RESULTS

The perfect-pairing procedure yields for the interaction energy of a system⁶

$$V = \sum_{\text{paired orbitals}} J_{ij} - \frac{1}{2} \sum_{\text{nonpaired orbitals}} J_{ij} - \sum_{\text{orbitals with parallel spins}} J_{ij} \quad (1)$$

if one neglects Coulombic terms which should be small at large distances. Here J_{ij} is the exchange integral involving the orbitals i and j . Equation (1) immediately yields for the interaction energies between two ground-state H atoms

$$\begin{aligned} V(^1\Sigma) &= +J, \\ V(^3\Sigma) &= -J. \end{aligned} \quad (2)$$

For the interaction between H atoms in *different* molecules, however, where spins are randomly oriented with respect to one another, one obtains

$$V(\text{H} \cdots \text{H}) = -\frac{1}{2}J. \quad (3)$$

Following the procedure we have used in the past,⁷⁻¹⁰ we evaluated J from a knowledge of the interaction curve for the ³Σ state, and used this same J to obtain

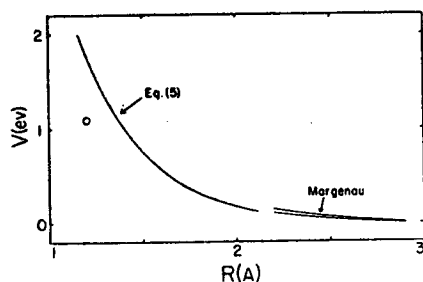


FIG. 1. Interaction energies for the H-H₂ system. The curve indicated by Eq. (5) was calculated by the perfect-pairing procedure. The two curves at larger distances are Margenau's calculated curves for the linear and triangular configurations, the upper curve being due to the linear one. The circle corresponds to a point on the H-H₂ curve obtained from scattering data on the H⁻-H₂ system.

⁷ J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, J. Chem. Phys. **30**, 129 (1959).

⁸ J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. **31**, 738 (1959).

⁹ J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. **32**, 515 (1960).

¹⁰ J. T. Vanderslice and E. A. Mason, Revs. Modern Phys. **32**, 417 (1960).

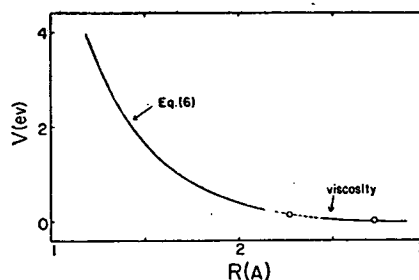


FIG. 2. Interaction energies for the H₂-H₂ system. The curve indicated by Eq. (6) was calculated by the perfect-pairing procedure. The curve marked "viscosity" was obtained from high-temperature viscosity measurements. The dashed part of this latter curve is an extrapolation. The circles are Evett and Margenau's calculated results.

$V(\text{H} \cdots \text{H})$ by Eq. (3). We have taken the expression for $V(^3\Sigma)$ from footnote reference 5. This yields

$$V(\text{H} \cdots \text{H}) = 30.21e^{-3.013r} \text{ ev}, \quad 0.8 \text{ Å} < r < 2.1 \text{ Å}. \quad (4)$$

The interaction between an atom and a molecule or between molecules is then, consistent with the perfect-pairing approximation, just the sum of all the separate interactions. The results of course depend on the relative orientations of the approaching species. Many times, it is useful to have potentials averaged over orientations for purposes of comparison with experimental results. The methods of averaging have been summarized previously for cases where all orientations are equally probable.⁷ Application of this procedure gives for the H-H₂ interaction,

$$\langle V(R) \rangle = 61.5e^{-2.952R} \text{ ev}, \quad 0.86 \text{ Å} < R < 2.12 \text{ Å}, \quad (5)$$

and for the H₂-H₂ interaction,

$$\langle V(R) \rangle = 116.5e^{-2.859R} \text{ ev}, \quad 0.91 \text{ Å} < R < 2.14 \text{ Å}, \quad (6)$$

where R is the distance between the centers of mass of the species.

These curves are plotted in Figs. 1 and 2, respectively. The H-H₂ curve can be compared with the first-order perturbation results of Margenau,¹¹ who calculated the interaction energy for both the linear and triangular cases. His results are shown in Fig. 1. Equation (5) can also be compared with one point (indicated by the circle in Fig. 1) on the H-H₂ curve obtained indirectly from the scattering of H⁻ ions in H₂.¹² It is seen to fall below the curve given by Eq. (5). There are two likely reasons for this. First, this point is not unambiguously determined because of the difficulty in interpreting the experimental results.¹² Secondly, our averaging assumes that all orientations are equally probable, which is certainly not the case at distances of the order of 1 Å.

The H₂-H₂ potential can be compared at larger dis-

¹¹ H. Margenau, Phys. Rev. **66**, 303 (1944); **64**, 131 (1943).

¹² E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **28**, 1070 (1958).